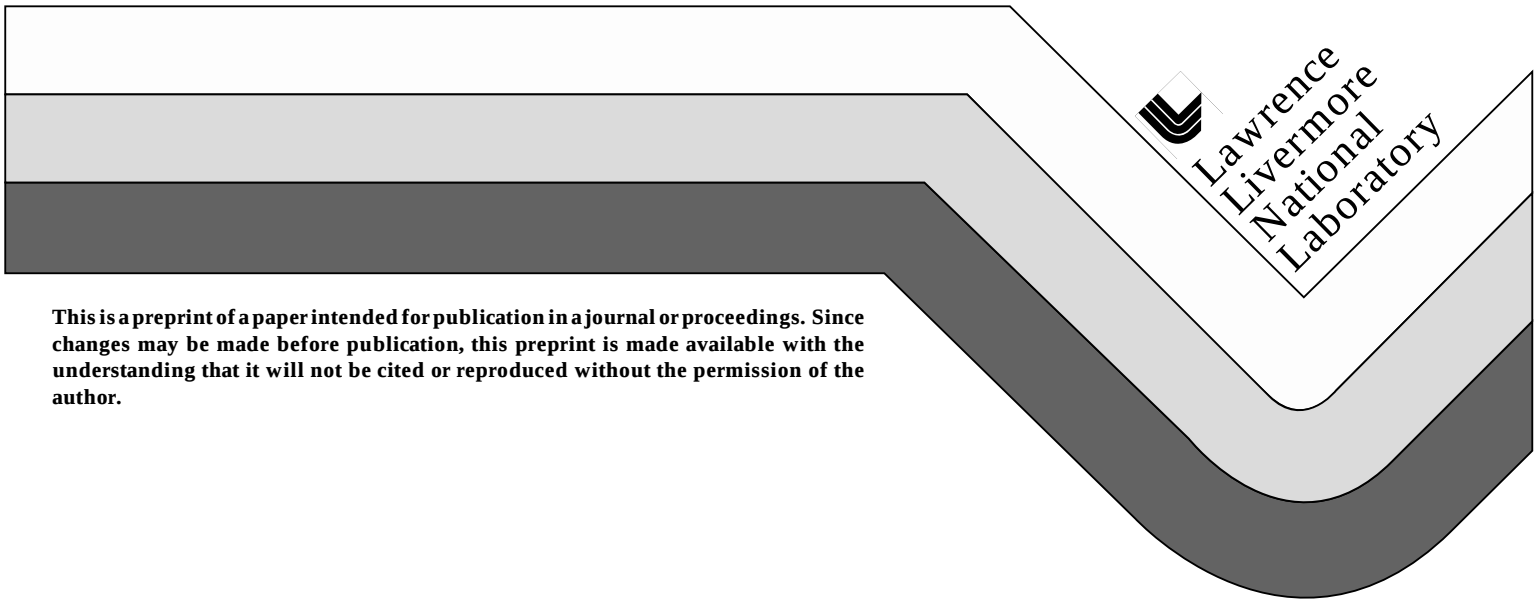
UCRL-JC-124043
PREPRINT

Status of Immobilization for Disposition of Surplus Fissile Materials

L. W. Gray
T. Kan

This paper was prepared for submittal to the Symposium XIII Environmental Issues and Waste Management Technology in Ceramic and Nuclear Industry Indianapolis, IN April 15, 1996

May 10, 1996



STATUS OF IMMOBILIZATION FOR DISPOSITION OF SURPLUS FISSILE MATERIALS

Leonard W. Gray
Lawrence Livermore Nat'l. Lab.
P.O. Box 5508, L-592
Livermore, CA 94550
(510) 422-1554

Tehmau Kan
Lawrence Livermore Nat'l. Lab.
P.O. Box 5508, L-592
Livermore, CA 94550
(510) 422-6160

ABSTRACT

The safe management of surplus weapons plutonium is a very important and urgent task with profound environmental, national, and international security implications. In the aftermath of the Cold War, Presidential Policy Directive 13 and various analyses by renown scientific, technical, and international policy organizations have brought about a focused effort within the U.S. Department of Energy to identify and implement options regarding the long-term disposition of surplus weapons usable plutonium. The primary goal is to render surplus weapons plutonium as inaccessible and unattractive for reuse in nuclear weapons, as the much larger and growing stock of plutonium contained in civilian spent reactor fuel. One disposition alternative considered for surplus plutonium is immobilization, in which plutonium would be emplaced in glass or ceramic.

INTRODUCTION AND SUMMARY

In the aftermath of the Cold War, the U.S. and Russia agreed to large reductions in nuclear weapons. Although disarmament offers hope for improving world security, disposition of plutonium used in nuclear weapons may also have significant international security implications if not managed properly. To aid in the selection of long-term management options, the U.S. Department of Energy (DOE) has undertaken a study to select options for storage and disposition of plutonium in keeping with the national policy that excess plutonium must be subjected to the highest standards of safety, security, and international accountability. Disposition is defined as a process of use or disposal of materials that results in the remaining material being converted to a form substantially and inherently more proliferation-resistant than the original form. Disposition options must take into

account technical, nonproliferation, environmental, budgetary, and economic considerations. As a collaborative endeavor, Russia and other nations with relevant interests and experience have been invited to participate in the overall disposition study.

One disposition alternative considered for surplus plutonium is immobilization.[1] Immobilization would embed plutonium in a tailored ceramic,[2,3] glass,[4] or other suitable material,[5] alone or mixed with radioactive fission products to produce a suitable disposal form. To be viable, the plutonium concentration of the form must be in the range of 1.0 to 10 wt% range.

Lawrence Livermore National Laboratory (LLNL) was selected as the lead laboratory by the Fissile Materials Disposition (MD) Office of the DOE to study and recommend methods for transformation of surplus fissile materials (SFM) (primarily plutonium) into long-term immobilized forms. These methods must meet the following requirements: to meet environmental, safety, and security objectives; to provide appropriate input to other disposition task teams to assess technical feasibility of immobilization as a long-term disposition option; and to describe infrastructures required to conduct disposition of SFM. Support laboratories include Westinghouse Savannah River Technology Center, Argonne National Laboratory, Oak Ridge National Laboratory, Pacific Northwest Laboratory, and the Australian Nuclear Science and Technology Organization (ANSTO).

An important consideration in evaluating disposition options for surplus plutonium is the “spent fuel standard.” This term, which was coined by the U.S. National Academy of Sciences[6] (NAS), is described as follows: “. . . disposition of weapons plutonium should seek to meet a ‘spent fuel standard’—that is, to make this plutonium roughly as inaccessible for weapons use as the much larger and growing quantity of plutonium that exists in spent fuel from commercial reactors.”

According to the NAS,[7] “this concept was not intended to imply a specific combination of radiation barrier, isotopic mixture, and degree of dilution of plutonium but rather to denote a condition in which the plutonium has become roughly as difficult to acquire, process, and use in nuclear weapons as it would be to use plutonium in commercial spent fuel for this purpose.”

SELECTION OF WASTE FORMS AND PROCESSING ALTERNATIVES FOR IMMOBILIZING PLUTONIUM

We selected five base case alternatives comprising glass[4,8,9] and ceramic[2,3,8,9] forms out of the 72 waste forms identified in a literature search[10] to be evaluated as potential vehicles for immobilizing plutonium. Table 1 addresses their different characteristics; Figs. 1 and 2 illustrate their implementation.

Table 1. Characteristics of glass and ceramic alternatives.

Glass	Ceramic
Internal Radiation Barrier: **Alternative 1:** A new greenfield facility that produces a borosilicate glass containing plutonium, neutron absorbers, and 137Cs (as a radiological barrier), and then encapsulates this glass in a storage canister. **Alternative 2:** An adjunct melter to the existing Defense Waste Processing Facility (DWPF) that produces a glass containing plutonium, neutron absorbers, and high level waste (HLW), and then encapsulates this glass in a storage canister.	**Internal Radiation Barrier:** **Alternative 1:** A new greenfield facility that produces a ceramic containing plutonium, neutron absorbers, and 137Cs and then encapsulates the ceramic in a storage canister.
External Radiation Barrier: **Alternative 1:** A “can-in-canister” variant, in which an inner can containing a plutonium and neutron-absorber-bearing glass is surrounded by a glass containing a radiological barrier, which is then contained in an outer storage canister.	**External Radiation Barrier:** **Alternative 1:** A “can-in-canister” alternative in which an inner can of a ceramic containing plutonium and neutron absorbers is surrounded by a glass that contains a radiological barrier, which is then contained in an outer storage canister.

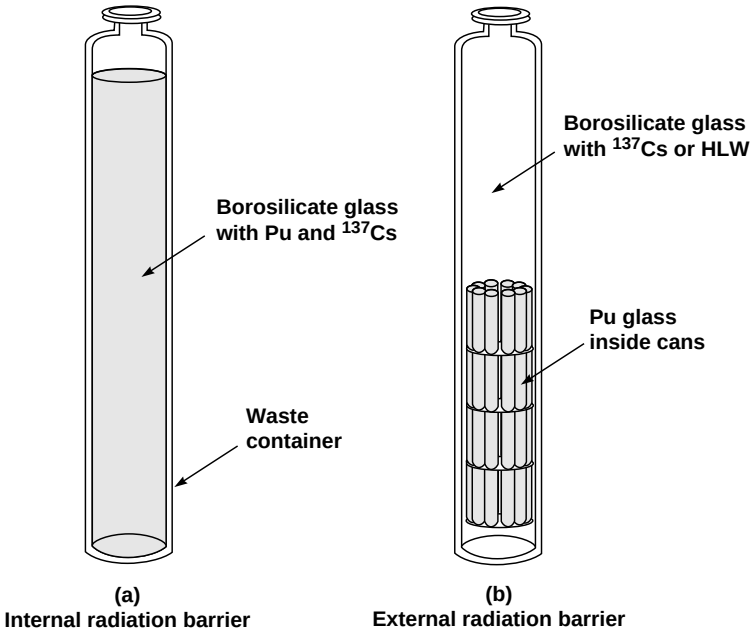


Figure 1. Options for vitrification of plutonium in glass.

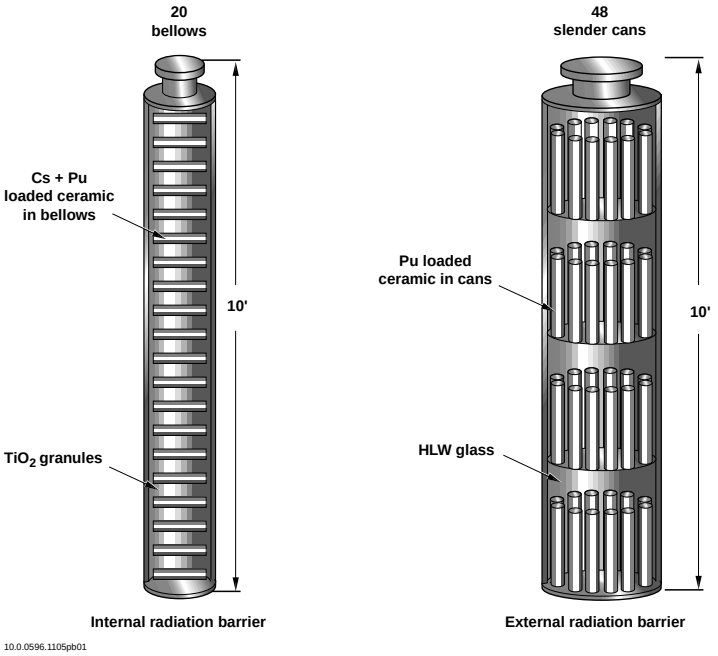


Figure 2 Options for immobilizing plutonium in a ceramic.

New Facility Alternatives

Preconceptual designs for the five alternatives have been analyzed. For either the glass or the ceramic facility,[11] input feed materials are first processed into PuO_2 by equipment located in glove boxes. In the glass facility, the oxide is fed to a first stage melter which produces plutonium glass frit. The frit is then processed in the second melter, along with ^{137}Cs, to produce the immobilization form within a canister. In a ceramic facility, the oxide is slurried with ceramic precursors, along with ^{137}Cs, is calcined, and then hot pressed within a bellows to produce the immobilization form which is then loaded into the canister. Neutron absorbers, such as gadolinium, samarium or hafnium, are also added to the immobilization form feed stream for criticality control. After interim storage, the canisters are transported for disposal in the Federal geologic repository.

Existing Facilities Alternatives

Existing structures and processing facilities at the Savannah River Site (SRS) are also being considered for immobilization of plutonium.[12] The Defense Waste Processing Facility (DWPF) has been considered for both vitrification of plutonium and as a means to provide a radiation barrier, surrounding the plutonium immobilized form. Introduction of plutonium into the DWPF processing stream and incorporating the plutonium within the HLW glass matrix would require significant modifications and upgrades to the facility. These actions would have significantly impacted the schedule for the primary DWPF mission which is to vitrify HLW stored in tanks at SRS. A more attractive option is to make a plutonium glass and place it into small cans, which is then put into a DWPF canister, using the processing facilities within the 221-F complex at SRS. These canisters would then be transported to DWPF and filled with DWPF glass. The HLW glass provides additional proliferation resistance in the form of a radiation field. With this alternative there is no change in the feed preparation or glass production process in DWPF, and, therefore, has minimal impact on the primary mission of DWPF. Another alternative employing this general approach is to immobilize the plutonium in a ceramic, encapsulate the ceramic in small cans or rods, and then place these cans or rods into a DWPF canister.

Prior to the introduction of HLW into the DWPF facility, a full-scale demonstration of the can-in-canister concept was completed, using 8 and 20 cans placed into the canister. Full nondestructive and destructive analyses of these canisters and full thermal analysis and modeling effort is being conducted by LLNL, SRS, and the Amarillo National Resource Center for Plutonium.

Research and Development Features[13] and Future Requirements

The fundamental features of the long-term research and development (R&D) plan for plutonium disposition using immobilization technologies include:

- Full understanding of criticality safety margins at every stage of plutonium handling and processing.
- Practical limits of plutonium concentration from both solubility and kinetic considerations.
- Incorporation of ^{137}Cs and its effects on both process operations and final waste form performance and proliferation resistance.
- Sensitivity of immobilization process formulation and product performance to impurity concentrations in the feed. Process optimization to minimize waste, costs, and time of disposition.
- Pilot scale demonstrations with transuranics to confirm viability of the process.
- Evolving and characterizing equipment designs and compositions that reliably and safely handle plutonium weight loadings that result in economically effective operations.
- Properties that influence performance, reliability, and safety considerations must be determined.
- Assessments of the physical durability of the product and the plutonium product phases. Relative durability and leach rate determination.
- Assessments of plutonium recovery and proliferation resistance of the immobilized plutonium form.

- Development of predictive material control and accountability and process controls and models for plutonium immobilization operations.

Analytical tools and techniques will need to be properly validated. These issues have a large effect on process complexity and limitations on throughput, so it is imperative that a consistent set of baseline data be carefully and fully determined. The experimental work and other assessments identified in the R&D plan are intended to address these issues.

Each of the five technologies requires further research and development to:

1. Identify a material formulation that optimizes processibility and long-term performance;

2. Develop processing equipment, material flow and process controls, operational strategies, and material accountability; minimize impacts on workers, the environment, cost, and the ability to maintain an acceptable implementation schedule; and using a pilot-scale model, demonstrate that individual operations or processing steps fit together seamlessly.

3. Demonstrate that the specific disposal forms meet the spent-fuel standard for proliferation resistance.

PROGRESS TO DATE

Vitrification

Vitrification of plutonium is a dissolution process.[14] Glass-forming chemicals are mixed with PuO_2 and neutron absorbers and then heated to melting. Above the melting point, the glass forming chemicals dissolve the plutonium and neutron absorbers, incorporating them into the glass matrix. The melt is then poured into a canister, which is sealed for storage and disposal. Ideally, the glass product is homogeneous—it contains no separate phases, either crystalline or amorphous. Therefore, the glass former is the solvent, which is formulated to maximize PuO_2 and neutron absorber solubility along with other desirable properties (such as processibility, chemical durability, etc.).

The HLW glass composition that is under consideration in the U.S. is based on wastes that results from the reprocessing of spent reactor fuel. In general, the feed streams contain a range of components that are either glass formers or modifiers, but very little plutonium. These glasses, therefore, have been optimized to accommodate high loadings of compositionally complex wastes. Adaptation of these existing glasses to incorporate high concentrations of plutonium has not been required and thus only a limited data base is available for evaluating how much plutonium can be dissolved in glass. The work that has been done on plutonium solubility in glasses suggests that fairly high plutonium loadings (2 to 13 wt%) should be achievable.[15]

Since current HLW glasses are formulated to tolerate the nonradioactive components (Fe, Al, and Na) which dominate HLW, new glasses can be formulated to improve the solubilities of plutonium and neutron absorbers. Two glasses have been formulated by the program and show promise for the immobilization mission.

1. An alkali-tin-silicate glass has been developed that is capable of dissolving up to 7 wt% PuO_2, which after further development may be expected to go higher. Although test results are preliminary, they indicate that this glass avoids formation of clay minerals usually found as corrosion products of HLW glasses. It appears that the release of plutonium and gadolinium to solution is occurring congruently. The processing behavior of this formulation is yet to be tested. While it appears to readily form a glass at 1150˚C, the viscosity and volatility of cesium are not yet known.

2. A second formulation[14] is based on the commercial "Löffler" glasses. These optical glasses typically contain up to 55 wt% rare earth oxides. Since the chemistries of the actinides and the rare earths are often similar, the solubility of plutonium should also be high. Up to 20 wt% ThO_2 or UO_2 can be dissolved in this glass and more than 10 wt% plutonium has been dissolved in these glasses.

Ceramics

Immobilization of plutonium in a crystalline ceramic is best thought of as a replacement of atoms within the mineral crystal lattice of a continuous solid solution. Mineral forming oxides (ceramic precursors) are mixed with PuO_2 and neutron absorbers, and then hot

pressed in stainless steel bellows.[16] For the immobilization of plutonium, the mineral form does not consist of a single phase; the baseline composition assumed is a mixture of zirconolite (~80%), hollandite (~15%), and rutile (~5%), if cesium is present; and zirconolite (~90%) and rutile (~10%), if cesium is not present in the immobilization form. Zirconolite is the plutonium host phase; hollandite is the cesium host phase. In this ceramic formulation, plutonium can replace zirconium as Pu(IV) or calcium as Pu(III).

The titanate-based immobilization form for HLW was developed in 1975. In 1978, Ringwood[17] proposed the Synthetic Rock concept, which relied heavily upon mineralogical compatibilities exhibited in nature. Although the initial formulation was not very successful, a later formulation, composed primarily of zirconolite, perovskite, hollandite, and rutile was very successful. From 1980 to 1983, an intense research program was dedicated to the study of various immobilization forms including synthetic rock, for defense HLW. With the selection of borosilicate glass in the early 1980s as the preferred HLW form, research on ceramic immobilization forms diminished in the U.S. At the ANSTO, however, development continued with the completion of the Synroc demonstration plant in 1987. Since then, the plant has operated on various short campaigns to demonstrate full scale Synroc processing using surrogate HLW solutions, fabricating over 6000 kg of Synroc at commercial scales of about 10 kg/hr.[18] If a fine-grained precursor material is used, and if the waste materials are loaded as nitrates, as it would be in a commercial reprocessing plant, then a homogenous and fully reacted product with densities greater than 98% of theoretical is routinely achieved by hot pressing at about 15MPa and 1150˚C .

The best demonstrated process for ceramic fabrication, particularly ceramic with an internal radiation barrier, is hot-pressing in bellows. This process had previously been demonstrated at full-scale (~30 kg) with HLW surrogates and at small laboratory scale with plutonium (10 to 20 g total mass). LLNL built and installed a hot press capable of producing ~0.5 kg ceramic in 7.5 cm diam bellows that was fully operational in January 1996. At that time, the first ceramic product containing up to about 60 grams of plutonium was produced.

SUMMARY

An international team was assembled for the purpose of selecting suitable immobilization forms and processing technologies for the Fissile Materials Disposition Program Office. As a reference point, the team used the NAS Study but did not limit their recommendations to those of the NAS. As a result, two basic forms were selected and the processing alternatives to provide those two forms were defined. Environmental data have been supplied to support a preliminary environmental impact statement for the disposition program. Cost data for the Record of Decision, which is anticipated in the Fall of 1996, is being developed.

The immobilization program has also entered the R&D Phase and progress has been made on the formulation of both glass and ceramic forms. Samples of both glass and ceramics containing tens of grams of plutonium have been prepared which indicate that the required concentration range can be obtained. Long-term leach tests to verify performance requirements in the repository are also under way.

ACKNOWLEDGMENT

This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily reflect any biases, proposed actions, or decisions of the United States Government or any agency thereof.

REFERENCES

1. U.S. Department of Energy, “Summary Report of the Screening Process to Determine Reasonable Alternatives for Long-Term Storage and Disposition of Weapons-Usable Fissile Materials,” DOE/MD-002, Washington, DC, March 29, 1995.

2. L. W. Gray et al., “Fissile Materials Disposition Program, PEIS Data Call Input Report: Ceramics Immobilization Facility with

Radionuclides," UCRL-ID-122665, Lawrence Livermore National Laboratory, Livermore, CA, February 9, 1996.

3. L. W. Gray et al., "Fissile Materials Disposition Program, PEIS Data Call Input Report: Ceramics Immobilization Facility, Using Coated Pellets without Radionuclides," UCRL-ID-122666, Lawrence Livermore National Laboratory, Livermore, CA, February 9, 1996.

4. L. W. Gray et al., "Fissile Materials Disposition Program, PEIS Data Call Input Report: New Glass Vitrification Facility," UCRL-ID-122658, Lawrence Livermore National Laboratory, Livermore, CA, February 9, 1996.

5. L. W. Gray et al., "Fissile Materials Disposition Program, PEIS Data Call Input Report: Immobilization of Surplus Fissile Materials with Electrometallurgical Treatment of Spent Fuels," UCRL-ID-122667, Lawrence Livermore National Laboratory, Livermore, CA, February 9, 1996.

6. National Academy of Sciences, "Management and Disposition of Excess Weapons Plutonium," National Academy Press, 1994.

7. National Academy of Sciences, "An Evaluation of the Electrometallurgical Approach for Treatment of Excess Weapons Plutonium," National Academy Press, 1995.

8. L. W. Gray and T. Kan, "Safety Aspects with Regards to Plutonium Vitrification Techniques," to be published in the Proceedings of the NATO conference on "Disposal of Weapons Plutonium," St. Petersburg, Russia, May 14–17, 1995.

9. L. W. Gray, T. Kan, W. G. Sutcliff, J. M. McKibben, and W. Danker, "Disposition of Surplus Fissile Materials via Immobilization," Vol. XXIV, 413, Institute of Nuclear Materials Management 36th Annual Meeting Proceedings, Palm Desert, CA, July 9–12, 1995.

10. L. W. Gray, et al. "Screening of Alternate Immobilization Candidates for Disposition of Surplus Fissile Materials," UCRL-ID-118819 , Lawrence Livermore National Laboratory, Livermore, CA, February 9, 1996.

11 T. Kan and K. Sullivan, “Glass and Ceramic Immobilization Alternatives and the Use of New Facilities,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.

12 J. B. Duane et al., “Use of Savannah River Site Facilities for Glass and Ceramics,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.

13. L. Gray, T. Kan, H. Shaw, and G. Armantrout, “Immobilization Needs and Technology Programs,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.

14. M. J. Plodinec, et al., “Survey of Glass Plutonium Contents and Poison Selection,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.

15. J. Bates, et al., “Glass Corrosion and Irradiation Damage Behavior,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.

16. B. B. Ebbinghaus, et al., “Status of Plutonium Ceramic Immobilization Processes and Immobilization Forms,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.

17. A. E. Ringwood, “Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy,” Australian National University Press, Canberra, 1978.

18. A. Jostsons, et al., “Experience Gained with Synroc Demonstration Plant at ANSTO and its Relevance to Plutonium Immobilization,” Plutonium Stabilization & Immobilization Workshop, December 12–14, 1995, Washington DC, U.S. Department of Energy, March, 1996.